

The University of Chicago

STUDIES OF CONJUGATED SYSTEMS

- I. THE ADDITION OF BROMINE, HYDROGEN BROMIDE AND HYPOBROMOUS ACID TO 1-BROMOBUTADIENE
- II. THE PREPARATION AND PROPERTIES OF 1-PHENYL-4-BROMOBUTADIENE
- III. THE PREPARATION AND PROPERTIES OF 1-PHENYL-4-AMINO-BUTADIENE AND 1-PHENYL-4-ANILIDOBUTADIENE

A DISSERTATION SUBMITTED TO THE FACULTY OF THE
DIVISION OF THE PHYSICAL SCIENCES IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1933

BY
LOREN BENJAMIN GRIMSLEY

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Studies of Conjugated Systems. I. The Addition of Bromine, Hydrogen Bromide and Hypobromous Acid to 1-Bromobutadiene

In the course of an extended investigation of the properties and reactions of conjugated systems Muskat and his co-workers¹ have developed a theory of the electronic configuration and addition reactions of conjugated compounds which has proved very useful in interpreting a large number of heretofore anomalous reactions of these compounds. This theory is based on the supposition that conjugated systems differ from non-conjugated systems only in so far as the former may exhibit 1,3-rearrangement, while the latter cannot exhibit this phenomenon. It further assumes that the addition of both components of the addendum to an ethylenic double bond need not occur simultaneously, but rather, as has been suggested by Stieglitz,² that the essential feature is the attraction of the positive substituting group to the negative carbon valencies irrespective of complete saturation.³

Ingold and his collaborators⁴ have developed a somewhat similar theory to interpret the addition reactions of conjugated systems. As a direct consequence of their theory Ingold and Smith⁵ predicted that 1-bromobutadiene would add halogens and halogen acids in the 3,4-positions similar to 1-phenylbutadiene. Consequently they studied the addition of bromine and hydrogen bromide to 1-bromobutadiene and reported that 3,4-addition had taken place in each instance. Previous to the publication of this work we had begun an investigation of the addition of bromine, hydrogen bromide, and hypobromous acid to 1-bromobutadiene. Our results are in contradiction to those reported by Ingold and Smith, for we were able to prove definitely that bromine, hydrogen bromide, and hypobromous acid add to 1-bromobutadiene in the 1,4-positions.

Applying the principles developed by Muskat and Northrup⁶ for the addition reactions of conjugated systems, to the bromination of 1-bromobutadiene, we would have as the first step of the reaction the addition of

(1) Muskat and Becker, *J. Am. Chem. Soc.*, **52**, 812 (1930); Muskat and Northrup, *ibid.*, **52**, 4043 (1930); Muskat and Knapp, *Ber.*, **64**, 779 (1931); Muskat and Hudson, *J. Am. Chem. Soc.*, **53**, 3178 (1931); Muskat and Herrman, *ibid.*, **54**, 2001 (1932).

(2) Stieglitz, *ibid.*, **44**, 1304 (1922).

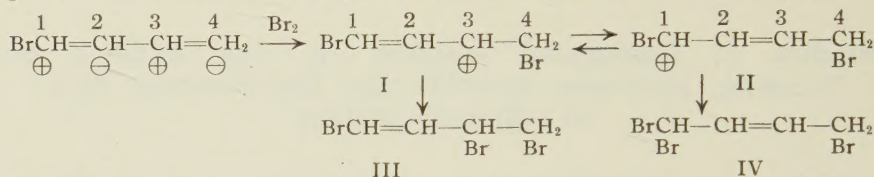
(3) In some cases, as in the reduction of conjugated compounds with sodium amalgam and similar reducing agents [see Muskat and Knapp, *Ber.*, **64**, 779 (1931)], it is the negative valencies which are first attacked.

(4) Ingold, *et al.*, *J. Chem. Soc.*, 910 (1928); *ibid.*, 2022 (1929); *ibid.*, 2752 (1931).

(5) Ingold and Smith, *ibid.*, 2752 (1931).

(6) Muskat and Northrup, *J. Am. Chem. Soc.*, **52**, 4049 (1930).

the positive bromine atom to the 4-carbon atom to give I.⁷ In the second phase of this reaction the negative bromine atom may satisfy the positive



charge on carbon atom 3 to give III, 3,4-dibromide of 1-bromobutadiene, in a manner normal to ordinary ethylenic compounds; or the intermediate I may undergo a typical 1,3-rearrangement to II, and the negative bromine atom could now add to the 1-carbon atom to give IV, 1,4-dibromide of 1-bromobutadiene. The formation of either the 1,4- or 3,4-isomer depends on the equilibrium of the two intermediates, I and II. This equilibrium in turn depends on the relative effects of the groups Br- and CH₂Br-, and upon the experimental environment in promoting or hindering this 1,3-rearrangement. Now if the effect of the CH₂Br group in promoting such a rearrangement is greater than the effect of the Br group in retarding this rearrangement, then we should expect bromination to occur mostly in the 1,4-positions. These are exactly the results we obtained. Of course the addition of hydrogen bromide and hypobromous acid may be explained in a similar manner.

The addition of bromine to 1-bromobutadiene was studied first. It was found that one mole of bromine was readily absorbed to give a dibromide addition product distilling at 94° under 8 mm. pressure. The bromination was effected in ligroin, chloroform and acetic acid solutions and in each case the same dibromide addition product was isolated. The structure of the dibromide addition product was determined by oxidation. Three dibromide addition products are theoretically possible, depending on whether 1,2-, 1,4-, or 3,4-addition takes place. If 1,2-addition occurs then on ozonization and subsequent hydrolysis formaldehyde, 1,2,2'-tribromopropionic aldehyde or their respective acids should be formed. If 1,4-addition occurs then on ozonization and subsequent hydrolysis bromoacetaldehyde, dibromoacetaldehyde (or rather, its hydrolysis and oxidation products, glyoxalic acid and oxalic acid) or their respective acids should be formed. If 3,4-addition occurs then bromoformaldehyde (or rather its decomposition products), 1,2-dibromopropionic aldehyde or their respective acids should be formed.

The dibromide addition product was oxidized both with ozone and with potassium permanganate in acetone solution, and in each case bromoacetic acid was the main product. Oxalic acid was also isolated in some of the

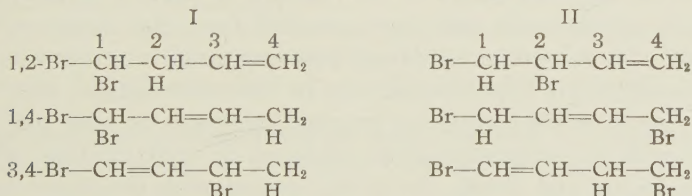
(7) The plus and minus signs do not imply a complete transfer of an electron from one atom to another. They indicate merely a displacement of the electrons from their central positions. We propose to use the encircled plus and minus signs to differentiate them from ionic charges.

ozonization experiments, and qualitative tests for glyoxalic acid were obtained. In not one of the large number of oxidation experiments that were performed were we able to detect any formaldehyde, 1,2-dibromopropionic aldehyde or bromoacetaldehyde. This proves that 1-bromobutadiene absorbs bromine in the 1,4-positions to give 1,1',4-tribromo- Δ^2 -butene, rather than in the 3,4-positions to give 1,3,4-tribromo- Δ^1 -butene as claimed by Ingold and Smith. As evidence for their structure Ingold and Smith state that they obtained carbon monoxide, hydrogen bromide and 1-bromoacetaldehyde. The 1-bromoacetaldehyde was identified by its carbon and hydrogen analysis (no bromine analysis is given), which is the same for oxalic acid, one of the products we isolated. However, they prepared a semicarbazone derivative which melted at 160° , the melting point of the semicarbazone of 1-bromoacetaldehyde, and a mixture with the known semicarbazone also melted at 160° . This evidence is not so conclusive since the semicarbazone of 1-bromoacetaldehyde melts with decomposition.⁸

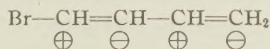
In order to make certain that no rearrangement occurred during the distillation, the bromination of the 1-bromobutadiene was effected at about -20° in low-boiling ligroin and the brominated product was immediately subjected to ozonization in the ligroin solution, the temperature being kept at -20° until the ozonization was completed. The same results reported above for the distilled product were again obtained.

The 1,1',4-tribromo- Δ^2 -butene absorbs a mole of bromine to give the same mixture of pentabromobutanes as reported by Willstätter and Bruce.⁹

The addition of hydrogen bromide to 1-bromobutadiene was then studied. The structure of the product was determined by ozonization. In this case six hydrogen bromide addition products are theoretically possible, depending on whether 1,2-, 1,4- or 3,4-addition takes place and also on the relative positions taken by the hydrogen and bromine groups.



Since 1-bromobutadiene most likely has the structure



we should expect that the hydrogen bromide addition product would have a structure as represented in Series I rather than in Series II. Also, as a result of our theoretical developments with regard to the addition

(8) Von Auwers and Müller, *Ann.*, **434**, 168 (1923).

(9) Willstätter and Bruce, *Ber.*, **40**, 3994 (1907).

reactions of conjugated systems, we should expect 1,4-addition to take place. The final proof of the structure of the hydrogen bromide addition product fully confirmed these views. On ozonizing the hydrogen bromide addition product it was possible to isolate both oxalic and acetic acids from the ozonized product. These acids could only result from the oxidation of a 1,4-addition product as represented in Series I. No trace of formaldehyde or brominated propionic acid derivatives which would result from the oxidation of 1,2- or 3,4-addition products, could be obtained. This proves that hydrogen bromide is absorbed in the 1,4-positions to give 1,1'-dibromo- Δ^2 -butene, rather than in the 3,4-positions to give 1,3-dibromo- Δ^1 -butene as claimed by Ingold and Smith.

The crude hydrogen bromide addition product was subjected to ozonization without any preliminary distillation in order to eliminate the possibility of rearrangement. The same oxidation products were isolated as with the pure distilled 1,1'-dibromo- Δ^2 -butene reported above.

The 1,1'-dibromo- Δ^2 -butene was dissolved in chloroform and one mole of bromine was added. The reaction was quite rapid. A product was obtained which distilled at 148–150° under 25 mm. pressure, and analysis showed it to be 1,1',2,3-tetrabromobutane.

Finally the addition of hypobromous acid to 1-bromobutadiene was studied. It was found that one mole of hypobromous acid was readily absorbed to give a product which upon analysis proved to be a mono-hypobromous acid addition product. Its structure was determined by ozonization. Again, as above with the hydrogen bromide addition product, six mono-addition products are theoretically possible, depending on whether 1,2-, 1,4- or 3,4-addition takes place and also on the relative positions taken by the bromine and hydroxyl groups. In this case 1,4-addition was expected to give 1,4-dibromo-1-hydroxy- Δ^2 -butene. This structure was fully confirmed by the isolation of oxalic acid and bromoacetic acid, which could only have resulted from the oxidation of this compound. No trace of any products which might have resulted from the 1,2- or 3,4-addition of hypobromous acid to 1-bromobutadiene were found.

These results on the addition of bromine, hydrogen bromide and hypobromous acid to 1-bromobutadiene, although in contradiction with the results of Ingold and Smith, are in full accord with the theoretical developments of Muskát and Northrup.⁶

Experimental Part

The Bromination of 1-Bromobutadiene.—1-Bromobutadiene was prepared according to the method of Willstätter and Bruce⁹ by the dry distillation of the 1,4-dibromide of butadiene with pulverized potassium hydroxide.¹⁰ The pure 1-bromobutadiene dis-

(10) Muskát and Northrup [*J. Am. Chem. Soc.*, **52**, 4055 (1930)] used the same method for the preparation of 1-chlorobutadiene. The boiling point of the 1-chlorobutadiene is 65–67° rather than 85° as stated on page 4055.

tils at 92–94° under atmospheric pressure. The theoretical amount of bromine (one mole) dissolved in low-boiling ligroin was added to the 1-bromobutadiene dissolved in ligroin. Absorption took place fairly rapidly and the reaction mixture became warm. The ligroin was removed by means of suction and the resulting oil was distilled under reduced pressure. A light colored oil was distilled over at 94° under 8 mm. pressure.

Anal. Calcd. for $C_4H_6Br_2$: Br, 81.91. Found: Br, 81.87, 82.20.

The conditions under which the 1-bromobutadiene was brominated were varied considerably. Various solvents such as ligroin, chloroform and glacial acetic acid were used and the temperature was varied from about –20° to about 50°. However, in all cases only one dibromide was obtained, regardless of the experimental conditions employed.

The 1-bromobutadiene dibromide, dissolved in dry carbon tetrachloride, was subjected to ozonization and the ozonide was decomposed with water. To assure complete decomposition, it was warmed on the water-bath for a short time. The mixture was free of aldehydes, as was shown by a negative fuchsin test. The water solution was extracted with ether a number of times, the ether extract was dried over anhydrous sodium sulfate and the ether was removed by means of suction. An oil remained which crystallized on standing. The crystals melted at 50°, the melting point of bromoacetic acid. A mixture with known bromoacetic acid also melted at 50°. The aqueous solution remaining from the ether extraction was carefully evaporated to dryness and further heated in the oven to 110° for several hours. The residue melted at 187°, the melting point of anhydrous oxalic acid. A mixture with pure oxalic acid also melted at 187°. The oxalic acid was further identified by a quantitative titration with standard potassium permanganate. A 43% yield of oxalic acid was isolated in one experiment. In some of the ozonization experiments color tests for glyoxalic acid with concentrated sulfuric acid were obtained.

The 1-bromobutadiene dibromide was also oxidized with potassium permanganate in acetone solution according to the method of Staudinger.¹¹ On working up the oxidized products as described by Staudinger, a considerable amount of bromoacetic acid was obtained which was identified as above.

In one experiment the 1-bromobutadiene was brominated in ligroin solution at –20°, and the ligroin solution at that temperature was directly subjected to ozonization without preliminary distillation. At no time was the temperature allowed to rise above –20°. On working up the oxidized product, both bromoacetic and oxalic acids were isolated and identified as above.

The 1-bromobutadiene dibromide absorbs one mole of bromine to give a mixture of pentabromobutanes. This mixture was identical with a mixture of pentabromobutanes obtained by Willstätter and Bruce by treating 1-bromobutadiene with an excess of bromine.⁹

The Addition of Hydrogen Bromide to 1-Bromobutadiene.—Dry hydrogen bromide, free from bromine, was passed directly into 1-bromobutadiene without the use of any solvent. Absorption took place fairly readily. If ether is used as a solvent, the absorption is very slow and incomplete. After one mole of hydrogen bromide had been absorbed, the dissolved hydrogen bromide was removed by means of suction and the resulting oil was distilled under atmospheric pressure. The largest part of the distillate came over at 155–157°. It was redistilled under 24 mm. pressure, the entire product distilling over at 71–72°. The product was analyzed soon after distillation, for decomposition occurs on standing.

Anal. Calcd. for $C_4H_6Br_2$: Br, 74.77. Found: Br, 74.54, 74.51.

The dibromobutene was dissolved in chloroform and subjected to ozonization. The

(11) Staudinger, *Helv. Chim. Acta*, **5**, 766 (1922).

ozonized product was worked up in a manner entirely analogous to the method described above for the 1-bromobutadiene dibromide. Both oxalic and acetic acids were isolated from the ozonized product. The oxalic acid was identified by its calcium salt and by titration with standard potassium permanganate. A 30% yield of oxalic acid was isolated in one experiment. The acetic acid was identified by its boiling point, formation of ethyl acetate with ethyl alcohol and sulfuric acid, the cacodyl test, and by the preparation of the *p*-toluide of acetic acid, m. p. 146°, which is the melting point of aceto-*p*-toluide. A mixture with a known product also melted at 146°.

In one experiment the crude hydrogen bromide addition product was subjected to ozonization without any preliminary distillation. At no time was the temperature allowed to rise above 0°. On working up the oxidized product, both acetic and oxalic acids were isolated and identified as above.

The 1,1'-dibromo- Δ^2 -butene was dissolved in chloroform and one mole of bromine was added. The reaction was quite rapid. The chloroform was removed by means of suction and the resulting oil was distilled under reduced pressure. The major portion distilled over at 148–150° under 25 mm. pressure. Its analysis showed it to be 1,1',2,3-tetrabromobutane.

Anal. Calcd. for $C_4H_6Br_4$: Br, 85.56. Found: Br, 85.32, 85.47.

The Addition of Hypobromous Acid to 1-Bromobutadiene.—The hypobromous acid was prepared by allowing bromine to drop slowly into a finely divided suspension of mercuric oxide in water at about –5°. A 1–2% solution of hypobromous acid, free from bromine, was used in these experiments.

1-Bromobutadiene was treated with the theoretical quantity of hypobromous acid solution. Absorption took place quite readily. The reaction product was extracted with ether, the solution was washed free of halides and dried over anhydrous sodium sulfate, and the ether was removed by means of suction. The resulting oil was analyzed and proved to be the bromohydrin of 1-bromobutadiene.

Anal. Calcd. for $C_4H_6OBr_2$: Br, 69.56. Found: Br, 69.56, 69.73.

The bromohydrin was dissolved in chloroform and subjected to ozonization. The ozonized product was worked up in a manner entirely analogous to the method described above. Both oxalic acid and bromoacetic acid were isolated from the ozonized product and they were identified exactly as described above for the 1-bromobutadiene dibromide.

Summary

1-Bromobutadiene absorbs bromine, hydrogen bromide and hypobromous acid in the 1,4-positions and not in the 3,4-positions as stated by Ingold and Smith. This is in direct accord with the theoretical developments of Muskat and his collaborators.

II. The Preparation and Properties of 1-Phenyl-4-bromobutadiene

While studying the preparation of conjugated amines it was found desirable to prepare 1-phenyl-4-bromobutadiene. Muskat and Huggins¹ had previously prepared the corresponding 1-phenyl-4-chlorobutadiene by treating the 3,4-dichloride of phenylbutadiene with aqueous potassium hydroxide, and we therefore attempted to use a similar method for the preparation of the bromo derivative. However, this reaction is much more complicated than it first appeared. On treating the 3,4-dibromide of phenylbutadiene with aqueous alkali there is formed some phenylbutadiene, tetrabromide of phenylbutadiene, styrylacetaldehyde, and an oily residue from which we were not able to isolate pure 1-phenyl-4-bromobutadiene. The monobromide, in contrast with the corresponding monochloride, could not be distilled without considerable decomposition, even under reduced pressure.

This peculiar reaction was investigated further and it was found that on treating the 3,4-dibromide of phenylbutadiene with almost any aqueous alkaline reagent, varying amounts of phenylbutadiene and tetrabromide of phenylbutadiene in corresponding molecular quantities are formed in addition to other products. If pyridine in non-aqueous solvents or a suspension of silver oxide in benzene is used, then both bromine atoms are removed to give phenylbutadiene. The expected elimination of hydrogen bromide to give 1-phenyl-4-bromobutadiene was not observed.

There is no apparent equilibrium between phenylbutadiene dibromide on the one hand and phenylbutadiene and the tetrabromide of phenylbutadiene on the other; for when phenylbutadiene and the tetrabromide of phenylbutadiene were treated with aqueous alkali under conditions similar to those that result in the formation of phenylbutadiene and the tetrabromide of phenylbutadiene from the 3,4-dibromide of phenylbutadiene, it was not possible to isolate any dibromide of phenylbutadiene.

The rate of bromination of phenylbutadiene was then studied and it was found that the first two atoms of bromine were absorbed almost instantly and exclusively in the 3,4-positions to give the 3,4-dibromide of phenylbutadiene, without the formation of even a trace of the tetrabromide of phenylbutadiene. After the first mole of bromine has been absorbed the rate of bromination decreases markedly and the second mole of bromine is absorbed slowly.

From the above study of the rate of bromination of phenylbutadiene it would seem that the 3,4-double bond is far more reactive toward bromination than is the 1,2-double bond; still, in the presence of aqueous alkali it appears that the 1,2-double bond of one molecule of the 3,4-

(1) Muskat and Huggins, *J. Am. Chem. Soc.*, **51**, 2496 (1929).

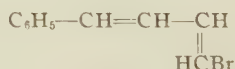
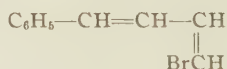
dibromide of phenylbutadiene absorbs the bromine from the 3,4-double bond of a second molecule of dibromide to give one molecule of phenylbutadiene and one molecule of tetrabromide of phenylbutadiene.² The corresponding chlorine derivatives show similar reactions but to a much less extent.

While studying the reaction of the 3,4-dibromide of phenylbutadiene with aniline in non-aqueous solvents, it was found that one or both of the bromine atoms could be replaced by the group $\text{—NHC}_6\text{H}_5$ but the elimination of hydrogen bromide to give 1-phenyl-4-bromobutadiene was not observed. If two molecules of aniline in benzene solution are added to one mole of the 3,4-dibromide of phenylbutadiene dissolved in benzene, reaction occurs quite readily with the formation of the monoanilide, which probably has the structure $\text{C}_6\text{H}_5\text{—CH=CH—CH(NHC}_6\text{H}_5\text{)—CH}_2\text{Br}$, and the elimination of aniline hydrobromide. If four moles of aniline are similarly added to one mole of the 3,4-dibromide of phenylbutadiene, the 3,4-dianilide of phenylbutadiene is formed.

The corresponding 3,4-diamine of phenylbutadiene resulted from the reaction of 3,4-dibromide of phenylbutadiene with a saturated solution of ammonia in 50% ethyl alcohol.

The 1-phenyl-4-bromobutadiene was finally prepared in almost quantitative yields by treating the 3,4-dibromide of phenylbutadiene with exactly one equivalent of alcoholic potash. The monobromide exists in two forms, probably *cis* and *trans* geometric isomers. One isomer is an oil, while the other is a solid melting at 52° .³ The solid isomer changes into the liquid isomer upon standing at room temperature.

The addition of hydrogen bromide to each of the geometric isomers of 1-phenyl-4-bromobutadiene was studied. It was found that each isomer absorbed one mole of hydrogen bromide in the 3,4-positions to give the same 3,4-dibromide of phenylbutadiene, with a melting point of 92° . This would indicate that the geometric isomerism of the 1-phenyl-4-bromobutadiene is due to the 3,4-double bond rather than to the 1,2-double bond.



However, this is not conclusive, for the two geometric isomers of phenylbutadiene in which the isomerism is due to the 1,2-double bond, give but one 3,4-dibromide of phenylbutadiene. The rate of bromination of the two geometric isomers of phenylbutadiene is quite different, the *cis*

(2) This statement is made, not as an explanation of the mechanism of this reaction, but simply as a statement of fact.

(3) This may be a transition point rather than a true melting point since the melt does not re-solidify, even when cooled to -10° .

isomer absorbing bromine more readily than does the *trans* isomer;⁴ still the same 3,4-dibromide is formed. Evidently the rearrangement occurs during bromination.

Due to the orientation of the hydrogen bromide in its addition to the 1-phenyl-4-bromobutadiene, it became of interest to determine the possible electropositive character of the bromine atom in the monobromide. The electropositive character of the bromine atom in the monobromide was indicated by the fact that it quite readily oxidized potassium iodide.

The addition of bromine to 1-phenyl-4-bromobutadiene was then studied. It was found that addition occurred in the 3,4-positions to give 1-phenyl-3,4,4'-tribromo- Δ^1 -butene. The position of the double bond was determined by ozonization.

From the experimental evidence presented, as well as from theoretical considerations, it appears that the electronic structure for 1-phenyl-4-

bromobutadiene is best represented⁵ as $\text{C}_6\text{H}_5-\overset{1}{\underset{\oplus}{\text{CH}}}=\overset{2}{\underset{\ominus}{\text{CH}}}-\overset{3}{\underset{\oplus}{\text{CH}}}-\overset{4}{\underset{\ominus}{\text{CH}}}\text{Br}$. Consequently, according to the theory developed by Muskat and his collaborators, the first step in the absorption of hydrogen bromide would be the addition of the positive hydrogen atom to the negative carbon atom (4) to give the intermediate $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\underset{\oplus}{\text{CH}}-\text{CH}_2\text{Br}$. This intermediate is

identical with the intermediate which was postulated for the bromination of phenylbutadiene⁶ and should therefore give the same product, namely, 1-phenyl-3,4-dibromo- Δ^1 -butene. This is in accord with the actual experimental results presented in this paper. The 3,4-addition of bromine to 1-phenyl-4-bromobutadiene may be explained in a similar manner.

Experimental Part

Rate of Bromination of the Geometric Isomers of Phenylbutadiene.—*Cis* and *trans* phenylbutadiene were prepared according to the method of Muskat and Herrman⁷ and the freshly distilled products were used in the bromination experiments. The rate of bromination of each of the geometric isomers was determined in chloroform solution at 0 and 25°. The phenylbutadiene was dissolved in chloroform and two moles of bromine also dissolved in chloroform were added. The reaction mixtures were maintained at the proper temperature by keeping the reaction vessels immersed in a constant temperature bath. Aliquot samples were removed at definite time intervals and titrated with standard sodium thiosulfate for unreacted bromine. The experimental data thus obtained for each of the geometric isomers are shown in Fig. 1.

(4) The *cis* phenylbutadiene is more rapidly hydrogenated and more rapidly oxidized than is the *trans* isomer. See Muskat and Knapp, *Ber.*, **64**, 779 (1931).

(5) The plus and minus signs do not imply a complete transfer of an electron from one atom to another. They indicate merely a displacement of the electrons from their central positions. We propose to use the encircled plus and minus signs to differentiate them from ionic charges.

(6) See Muskat and Northrup, *J. Am. Chem. Soc.*, **52**, 4049 (1930). In this paper the electronic explanation for the chlorination of phenylbutadiene is developed. The bromination of phenylbutadiene is similarly explained.

(7) Muskat and Herrman, *ibid.*, **53**, 252 (1931).

The 3,4-dibromide of each of the geometric isomers of phenylbutadiene was prepared. Since the geometric isomerism of phenylbutadiene must be due to the 1,2-double bond we expected to find two geometric isomers of the 3,4-dibromide of phenylbutadiene. However, only one product was obtained even though the bromination was carried out at about -80° . The identity of the two dibromides was determined by the melting point of mixtures and by the rate of bromination to the tetrabromides.

Reactions of the 3,4-Dibromide of Phenylbutadiene. In order to determine under what conditions the 3,4-dibromide of phenylbutadiene yielded phenylbutadiene and the tetrabromide of phenylbutadiene, a considerable number of experiments with

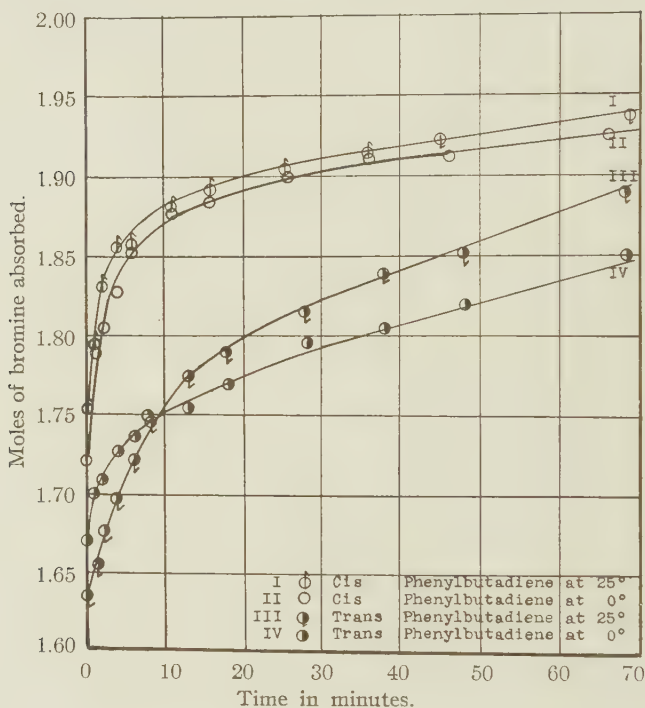


Fig. 1.

different aqueous alkaline reagents and under varying conditions as to temperature and time of reaction were performed. We shall list the results of only a few of these reactions.

Reagent	Temp., °C.	Time, min.	Bromide ion formed	Phenylbutadiene and tetrabromide of phenylbutadiene indicated
None	100	30	No	No
5% NaOH	0	60	No	No
5% NH_4OH	0	60	No	No
8% Pyridine	0	60	Yes	No
5% NaOH	100	25	Yes	Yes
10% NH_4OH	100	25	Yes	No
10% Pyridine	100	25	Yes	Yes

The tetrabromide of phenylbutadiene is much less soluble in low boiling ligroin (30–60°) than is the 3,4-dibromide of phenylbutadiene. Advantage was taken of this fact in detecting small amounts of the tetrabromide of phenylbutadiene in the presence of larger amounts of the 3,4-dibromide of phenylbutadiene, and conversely in detecting small amounts of the 3,4-dibromide of phenylbutadiene in the presence of larger amounts of the tetrabromide of phenylbutadiene. In this manner, 0.2 g. of tetrabromide was readily isolated and identified in the presence of much larger amounts of 3,4-dibromide of phenylbutadiene, and, conversely, 0.2 g. of 3,4-dibromide of phenylbutadiene was readily isolated and identified in the presence of much larger amounts of the tetrabromide of phenylbutadiene.

The 3,4-dibromide of phenylbutadiene was treated with a large excess of dry pyridine in benzene solution. The solution was heated on the water-bath for about twenty-four hours. The excess pyridine was neutralized with cold dilute hydrochloric acid and the resulting mixture was extracted with ether. The ether extract was washed free of acid and of halide ion and dried over anhydrous sodium sulfate. The ether was removed by means of suction and the residue was distilled under reduced pressure. A small amount of a light yellow oil distilled at 90° under 14 mm. pressure. This distillate was identified as phenylbutadiene by the melting point of its tetrabromide and the melting point of a mixture with a known sample of the tetrabromide of phenylbutadiene.

The 3,4-dibromide of phenylbutadiene, in benzene solution, was treated with silver oxide, and the suspension heated gently for about forty-eight hours. The reaction product was extracted with low boiling ligroin. Some crystals, which proved to be the unreacted dibromide rather than the tetrabromide of phenylbutadiene, were isolated. Distillation of the residue left by the removal of the solvent gave a small amount of a light yellow liquid, which distilled at 85° under 10 mm. pressure. This distillate was identified as phenylbutadiene by the melting point of its tetrabromide and by the melting point of a mixture with known tetrabromide of phenylbutadiene.

1-Phenyl-3-anilido-4-bromo- Δ^1 -butene.—The 3,4-dibromide of phenylbutadiene, in benzene solution, was treated with exactly two moles of aniline also in benzene solution, and the reaction mixture was allowed to stand at room temperature until there was no further precipitation of aniline hydrobromide. The reaction mixture was diluted with ether and washed with water to remove the bromide ion. The solution was dried over anhydrous sodium sulfate and the ether was removed by means of suction. A yellowish-orange crystalline mass remained which was soluble in benzene, chloroform, alcohol, and acetone. It melted at 110°.

Anal. Calcd. for $C_{16}H_{16}NBr$: Br, 26.49. Found: Br, 26.36, 26.36.

Although no effort was made to determine the position of the $—NHC_6H_5$ group, it is thought most likely to have the structure $C_6H_5—CH=CH—CH(NHC_6H_5)—CH_2Br$.

The 1-phenyl-3-anilido-4-bromo- Δ^1 -butene was dissolved in dry benzene and dry hydrogen bromide was passed into it. The hydrogen bromide salt was precipitated. The crystals were filtered off by means of suction, washed with anhydrous ether to remove the excess hydrogen bromide and, dried in a vacuum desiccator over anhydrous calcium chloride. These crystals were slightly yellow in color and hydrolyzed slowly when exposed to the air. The crystals melted at 124°.

Anal. Calcd. for $C_{16}H_{17}NBr_2$: Br, 41.78. Found: Br, 41.83, 41.75.

The compound is therefore the hydrobromide salt of the 1-phenyl-3-anilido-4-bromo- Δ^1 -butene.

The 1-phenyl-3-anilido-4-bromo- Δ^1 -butene was dissolved in chloroform and an excess of bromine was added. The crystals formed were filtered from the mother liquor, and washed several times with chloroform, leaving the crystals pure white. The crystals melted at 215°.

Anal. Calcd. for $C_{16}H_{14}NBr_7$: Br, 71.79. Found: Br, 71.70, 71.61.

The compound is therefore the hydrobromide salt of the 1-phenyl-1,2,4-tribromo-3-tribromoanilido-butane.

1-Phenyl-3,4-dianilido- Δ^1 -butene.—The 3,4-dibromide of phenylbutadiene was dissolved in benzene, four moles of aniline added, and the reaction mixture allowed to stand at room temperature until there was no further precipitation of aniline hydrobromide. The crystals of aniline hydrobromide were filtered off, the filtrate diluted with ether, washed free of bromide ion, and then dried over anhydrous sodium sulfate. Dry hydrogen chloride was then passed into the solution. The dihydrochloride salt of the dianilide was precipitated. The crystals were filtered off by means of suction, washed with anhydrous ether to remove the excess hydrogen chloride, and then dried in a vacuum desiccator over anhydrous calcium chloride. The crystals were slightly yellow in color and hydrolyzed slowly when exposed to the air. The crystals melted at 113° .

Anal. Calcd. for $C_{22}H_{24}N_2Cl_2$: Cl, 18.34. Found: Cl, 18.50, 18.45.

The compound is therefore the dihydrochloride salt of 1-phenyl-3,4-dianilido- Δ^1 -butene.

1-Phenyl-3,4-diamino- Δ^1 -butene.—The 3,4-dibromide of phenylbutadiene was dissolved in alcohol, the alcoholic solution treated with concentrated ammonium hydroxide and then gaseous ammonia passed into the reaction mixture to saturation. The reaction mixture was allowed to stand for six days at room temperature. It was then diluted with a large amount of water, extracted with ether, the ether extract washed free of ammonia and of bromide ion, and then dried over anhydrous sodium sulfate. Dry hydrogen chloride was passed into the solution. A white crystalline precipitate resulted. The crystals were filtered off by means of suction, washed with anhydrous ether to remove the excess hydrogen chloride, and then dried in a vacuum desiccator over anhydrous calcium chloride. The crystals were soluble in water, alcohol, acetone, and slightly soluble in ether. They melted at 124° and hydrolyzed only very slowly when exposed to the air.

Anal. Calcd. for $C_{16}H_{16}N_2Cl_2$: Cl, 30.18. Found: Cl, 30.22, 30.07

The compound is therefore the dihydrochloride salt of 1-phenyl-3,4-diamino- Δ^1 -butene.

1-Phenyl-4-bromobutadiene.—The 3,4-dibromide of phenylbutadiene was dissolved in ether and exactly one mole of alcoholic potassium hydroxide added. Sufficient alcohol was then added to prevent the separation of the reaction mixture into two layers, and it was then allowed to stand at room temperature until the mixture was neutral to litmus. Care should be taken to press the precipitated potassium bromide against the sides of the reaction vessel until quite granular so that it does not occlude any potassium hydroxide. The reaction mixture was then diluted with a large volume of water, extracted with ether, the ethereal extract washed several times with water, and then dried over anhydrous calcium chloride. The ether was removed by means of suction, without heating. There was left a residue of pure white, needle-like crystals, which even upon standing at room temperature slowly changed over to a light yellow, somewhat viscous oil. The crystals melted at 52° but did not recrystallize, even when cooled to -10° . The crystals were analyzed for bromine.

Anal. Calcd. for $C_{10}H_9Br$: Br, 38.23. Found: Br, 38.23, 38.15.

The oil was likewise analyzed for bromine.

Anal. Calcd. for $C_{10}H_9Br$: Br, 38.23. Found: Br, 37.90, 38.10.

Both compounds evidently have the structure 1-phenyl-4-bromobutadiene.⁸

An attempt to distil this oil resulted mainly in decomposition although a small

(8) The proof of the position of the bromine atom is given in Part III.

amount of a light yellow oil distilled at 137° under 6 mm. pressure. Analysis of this distillate for bromine showed it to be 1-phenyl-4-bromobutadiene. The residue left in the distilling flask was washed thoroughly with ether. A fine, light yellow powder remained.

Anal. Calcd. for $C_{10}H_9Br$: Br, 38.23. Found: Br, 38.37.

Molecular weight determinations indicate that the compound is a dimer of 1-phenyl-4-bromobutadiene. The compound melted at 138° .

Reactions of 1-Phenyl-4-bromobutadiene.—The liquid isomer of the 1-phenyl-4-bromobutadiene was dissolved in dry ether and dry hydrogen bromide was passed into the solution for about an hour. The ether was removed by means of suction and the crude crystals remaining were extracted with warm, low boiling ligroin. The crystals obtained from the ligroin extract melted at 92° , as did a mixture with a sample of known 3,4-dibromide of phenylbutadiene. The solid isomer of 1-phenyl-4-bromobutadiene also gave the same 3,4-dibromide of phenylbutadiene after being treated with hydrogen bromide in a similar manner.

A dilute potassium iodide solution was added to an aqueous suspension of 1-phenyl-4-bromobutadiene. Iodine was immediately liberated, showing that the potassium iodide was oxidized by the 1-phenyl-4-bromobutadiene. In order to obtain a rough estimate of the extent of the oxidation, the following experiment was conducted. Three grams of 1-phenyl-4-bromobutadiene, dissolved in a little ether, was added to an aqueous solution of potassium iodide and the mixture warmed on the water-bath to expel the ether. The reaction mixture was cooled and two or three drops of glacial acetic acid was added. The solution was then titrated with standard sodium thiosulfate for iodine. Assuming that the oxidation was due to the positive bromine atom in 1-phenyl-4-bromobutadiene, approximately 3% oxidation occurred in thirty hours. Of course, air was excluded during the entire reaction.

The 1-phenyl-4-bromobutadiene was dissolved in carbon tetrachloride and one mole of bromine also dissolved in carbon tetrachloride was added. The carbon tetrachloride was removed by means of suction. The viscous liquid which remained crystallized upon standing. The crude crystals were washed with small portions of low boiling ligroin. The compound, which was slightly gray in color, melted at $140-140.5^{\circ}$.

Anal. Calcd. for $C_{10}H_9Br_3$: Br, 65.04. Found: Br, 64.74, 64.70.

The compound is therefore the dibromide of 1-phenyl-4-bromobutadiene.

These crystals were dissolved in chloroform and a current of ozonized oxygen passed through the solution for about twenty-four hours. The chloroform was removed by means of suction and the residual ozonide decomposed with water. It was possible to isolate benzoic acid from the ozonization products. The benzoic acid was identified by its melting point and by the melting point of a mixture with known benzoic acid. The compound is therefore 1-phenyl-3,4,4'-tribromo- Δ^1 -butene.

Summary

1. The two geometric isomers of 1-phenyl-4-bromobutadiene were isolated.

2. Hydrogen bromide is absorbed by each of the geometric isomers of 1-phenyl-4-bromobutadiene in the 3,4-positions to give the same 3,4-dibromide of phenylbutadiene.

3. 1-Phenyl-4-bromobutadiene absorbs a mole of bromine in the 3,4-positions to give 1-phenyl-3,4,4'-tribromo- Δ^1 -butene.

4. The reactions of the 3,4-dibromide of phenylbutadiene with various alkaline reagents were studied and a number of new derivatives isolated.

III. The Preparation and Properties of 1-Phenyl-4-amino-butadiene and 1-Phenyl-4-anilidobutadiene

The characteristic properties and addition reactions of conjugated systems have been for some time the subject of an investigation in this Laboratory. One of the objects of this investigation was to throw some light on the mechanism of substitution and directive influence in the aromatic series. Some of the addition reactions of butadiene, phenyl-butadiene, carboxybutadiene, chloro- and bromobutadiene have already been studied and a theory has been developed¹ which explains these addition reactions without recourse to any special hypothesis of conjugation. In this paper we shall present the results of an investigation on the preparation and properties of aminobutadiene derivatives.

The aminobutadiene derivatives are the aliphatic analogs of the aromatic amines, such as aniline, diphenylamine and α -naphthylamine. Since the aromatic amines are among the most reactive as well as among the most important of aromatic compounds, a study of the aminobutadiene derivatives may not only throw some light on the reactions of aromatic amines, but may also prove of considerable interest for synthetic work. For instance, the diazotization and subsequent coupling reactions of these aminobutadiene derivatives would lead to a most interesting group of compounds. The aminobutadiene derivatives selected for this study were 1-phenyl-4-anilidobutadiene and 1-phenyl-4-aminobutadiene.

The 1-phenyl-4-anilidobutadiene was prepared by treating 1-phenyl-4-bromobutadiene with aniline. This reaction was carried out in various solvents in order to determine the conditions for optimum yield of the amine. It was found that the best yield was obtained when aniline was used as the solvent. The amine could not be distilled even under reduced pressure; there remained in the distilling flask a dimer of the amine which readily forms a monohydrochloride salt. No effort was made to prove the

structure of this dimer but the formula given is suggested. This formula would account for the

fact that only the monohydrochloride salt of the dimer is formed.

The reactions of this amine were then studied. When dry hydrogen chloride is passed into an anhydrous ether solution of the amine, the hydrogen chloride salt of 1-phenyl-4-anilidobutadiene is precipitated. This salt hydrolyzes when exposed to the atmosphere. When dry benzene is used as the solvent in place of ether, the dihydrochloride of 1-phenyl-4-anilidobutadiene is formed. This compound is the hydrogen chloride salt of what is probably 1-phenyl-3-chloro-4-anilido- Δ^1 -butene. This salt hydrolyzes only very slowly when exposed to the atmosphere. The 1-

(1) Muskat and Northrup, *J. Am. Chem. Soc.*, **52**, 4043 (1930).

phenyl-3-chloro-4-anilido- Δ^1 -butene was treated with an excess of chlorine in chloroform solution. 1-Phenyl-1,2,3-trichloro-4-trichloroanilidobutane hydrochloride was formed.

It was further found that the 1-phenyl-4-anilidobutadiene readily absorbs one mole of bromine to give 1-phenyl-3,4-dibromo-4-anilido- Δ^1 -butene. The structure of this compound was determined by ozonolysis. This dibromide absorbs a second mole of bromine to give 1-phenyl-1,2,3,4-tetrabromo-4-anilidobutane. On further treatment with an excess of bromine, 1-phenyl-1,2,3,4-tetrabromo-4-tribromoanilidobutane hydrobromide was formed. The 1-phenyl-4-anilidobutadiene absorbs likewise a mole of chlorine to give 1-phenyl-3,4-dichloro-4-anilido- Δ^1 -butene. The hydrogen chloride salt was precipitated when dry hydrogen chloride was passed into an ethereal solution of the dichloride.

The 1-phenyl-4-aminobutadiene was prepared by the interaction of alcoholic ammonia with 1-phenyl-4-bromobutadiene. An attempt to distil the amine under reduced pressure was not successful. When dry hydrogen chloride is passed into an ether solution of the amine, the hydrogen chloride salt is formed. This salt hydrolyzes when exposed to the atmosphere. If dry benzene is used as the solvent in place of the ether, the hydrochloride salt of what is probably 1-phenyl-3-chloro-4-amino- Δ^1 -butene is formed. This salt is hydrolyzed only very slowly under similar conditions.

It was likewise found possible to prepare the 1-phenyl-4-aminobutadiene by the reaction of sodium or potassium amide in liquid ammonia solution upon 1-phenyl-4-bromobutadiene, and also by the reaction of potassium phthalimide upon 1-phenyl-4-bromobutadiene, followed by the hydrolysis of the resulting product. It was further found possible to bring about the rearrangement of the acid amide of styrylacrylic acid to 1-phenyl-4-aminobutadiene by heating it with an aqueous solution of sodium hypochlorite.²

It is interesting to note that both the 1-phenyl-4-aminobutadiene and 1-phenyl-4-anilidobutadiene are stable in the amino form rather than in the imino form. This seems to emphasize the rather close analogy between the aliphatic conjugated compounds and aromatic compounds. Every effort to prepare aliphatic amines in which the amino group is attached to an unsaturated carbon atom has always yielded the corresponding imino derivatives or cyclic derivatives.³ In the case of vinylamine, there is some question as to its true structure. Gabriel,⁴ who first synthesized it, gave its structure as $\text{CH}_2=\text{CHNH}_2$. This was later disproved by Marckwald³ who favored the cyclic structure, $\begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ | \\ \text{NH} \end{smallmatrix}$. A number of the unsaturated amino derivatives have been given the imide structure, $\text{RCH}_2\text{CH}=\text{CHNH}_2$.

(2) The relation of these studies on the reactions of conjugated amines to the problem of substitution in the benzene ring will be discussed in a later paper.

(3) Marckwald, *Ber.*, **33**, 764 (1900); Howard and Marckwald, *ibid.*, **32**, 2031 (1899); Kohler and Drake, *J. Am. Chem. Soc.*, **45**, 1287 (1923).

(4) Gabriel, *Ber.*, **21**, 1049 (1888); Gabriel and Stelzner, *ibid.*, **28**, 2929 (1895).

NH.⁵ However, the 1-phenyl-4-aminobutadiene and 1-phenyl-4-anilidobutadiene are stable in the amino form just as is aniline. A number of attempts were made to hydrolyze both these amines but in no case were we able to detect ammonia or aniline in the hydrolytic products. The addition reactions of the 1-phenyl-4-anilidobutadiene and of 1-phenyl-4-aminobutadiene eliminate the possibility of the cyclic structure.

Experimental Part

1-Phenyl-4-anilidobutadiene.—1-Phenyl-4-bromobutadiene prepared according to the method of Muskat and Grimsley⁵ was treated with a large excess of aniline and allowed to stand at room temperature for twenty-four hours. The excess aniline was removed by treating with cold dilute hydrochloric acid. The resulting mixture was extracted several times with ether, the ether extract dried over anhydrous sodium sulfate and then over sodium hydroxide. The ether solution was filtered from the sodium hydroxide and dry hydrogen chloride was passed into the filtrate. A slightly yellow, crystalline precipitate was formed. The crystals were collected on a filter by means of suction, washed with dry ether to remove the excess hydrogen chloride, and then dried in a vacuum desiccator over phosphorus pentoxide. These crystals melted at 104–106° and hydrolyzed when exposed to the atmosphere. Due to this hydrolysis, the melting point may be somewhat low. The maximum yield, based upon the amount of the 1-phenyl-4-bromobutadiene which reacted, was 57%.

Anal. Calcd. for $C_{16}H_{15}NCl$: Cl, 13.74. Found: Cl, 13.81, 13.91.

This chlorine analysis indicates that the compound is the hydrogen chloride salt of 1-phenyl-4-anilidobutadiene.

The hydrogen chloride salt of 1-phenyl-4-anilidobutadiene was hydrolyzed with dilute aqueous alkali and the resulting mixture was extracted with ether. The ether solution was washed free of chloride ion and then dried first over anhydrous sodium sulfate and finally over sodium hydroxide. The ether was removed by means of suction. The free base, a dark red viscous oil, remained.

Anal. Calcd. for $C_{16}H_{15}N$: N, 6.33. Found: N, 6.21, 6.26.

These analyses show that the compound is 1-phenyl-4-anilidobutadiene.

1-Phenyl-4-chlorobutadiene, prepared according to the method of Muskat and Huggins,⁶ was treated with aniline in a manner exactly analogous to that described above for the corresponding bromo derivative. The hydrogen chloride salt of the anilide thus obtained was identical with the 1-phenyl-4-anilidobutadiene hydrochloride whose preparation from 1-phenyl-4-bromobutadiene was described above. Since the monochloride was definitely proved⁶ to have the structure $C_6H_5CH=CHCH=CHCl$, this constitutes definite proof of the similar structure of the corresponding monobromide.

An attempt to distil, under reduced pressure, the 1-phenyl-4-anilidobutadiene was not successful but there remained in the distilling flask a red rosin-like solid which was easily pulverized into an orange powder. This powder melted at 105°.

Mol. wt. Calcd. for $(C_{16}H_{15}N)_2$: mol. wt., 442. Found: mol. wt. (freezing point method, benzene), 446.

The powder was dissolved in benzene and dry hydrogen chloride was passed into the solution; a crystalline precipitate was formed. The crystals were collected on a filter by means of suction and washed with dry ether to remove the excess hydrogen chloride. These crystals melted at 152°.

Anal. Calcd. for $(C_{16}H_{15}N)_2HCl$: Cl, 7.41. Found: Cl, 6.80, 6.89.

(5) Muskat and Grimsley, *J. Am. Chem. Soc.*, **55**, 2860 (1933).

(6) Muskat and Huggins, *ibid.*, **51**, 2496 (1929).

Reactions of 1-Phenyl-4-anilidobutadiene

Addition of Hydrogen Chloride.—The 1-phenyl-4-anilidobutadiene was dissolved in dry benzene and dry hydrogen chloride passed into the solution while the container was immersed in an ice-bath. The solution became dark red in color but no precipitate was formed. Dry, low boiling ligroin (30–60°) was added dropwise to the solution and a chocolate brown crystalline material was precipitated. These crystals were collected on a filter by means of suction and washed with a small amount of warm benzene. The crystals which remained were slightly pink in color.

Anal. Calcd. for $C_{16}H_{17}NCl_2$: Cl, 24.12. Found: Cl, 24.03, 23.93.

The compound is the dihydrochloride of 1-phenyl-4-anilidobutadiene.

In order to determine the ionizable chlorine, the compound was dissolved in alcohol. An equal volume of water was added to precipitate the organic residue, and immediately filtered to avoid the hydrolysis of any loosely bound organic chlorine. The chloride ion was determined in the filtrate.

Anal. Calcd. for one ionizable chlorine in $C_{16}H_{17}NCl_2$: Cl, 12.06. Found: Cl, 12.58.

The compound is then the hydrogen chloride salt of the monohydrochloride addition product of 1-phenyl-4-anilidobutadiene.

These crystals melted at 124° and were hydrolyzed in contact with the atmosphere, but not as readily as was the hydrogen chloride salt of 1-phenyl-4-anilidobutadiene. The crystals are soluble in alcohol, acetone, chloroform, and to quite an appreciable extent in hot benzene.

This dihydrogen chloride derivative of 1-phenyl-4-anilidobutadiene was dissolved in chloroform and a current of ozonized oxygen passed into the solution for about twenty-four hours. The chloroform was removed by means of suction and the residual ozonide decomposed with water. It was possible to isolate benzoic acid from the ozonization products. The benzoic acid was identified by its melting point and by the melting point of a mixture with known benzoic acid. The hydrogen chloride has therefore been absorbed in the 3,4-positions of the 1-phenyl-4-anilidobutadiene. We did not determine the orientation of the hydrogen chloride in the 3,4-double bond but due to its reactions and also upon theoretical grounds we favor the formula 1-phenyl-3-chloro-4-anilido- Δ^1 -butene. In what follows, we shall use this formula although its structure was not proved.

The 1-phenyl-3-chloro-4-anilido- Δ^1 -butene hydrochloride was dissolved in chloroform, and a current of chlorine was passed into the solution until no more was absorbed. The chloroform was removed by means of suction. There remained a residue of slightly yellow crystals which were washed with ether to remove the color. The pure white crystals melted at 218°.

Anal. Calcd. for $C_{16}H_{14}NCl_7$: Cl, 53.00. Found: Cl, 53.17, 53.08.

The compound is 1-phenyl-1,2,3-trichloro-4-trichloroanilidobutane hydrochloride.

Addition of Bromine.—The 1-phenyl-4-anilidobutadiene was dissolved in chloroform and exactly one mole of bromine, dissolved in chloroform, was added. After the reaction was complete, the chloroform was removed by means of suction. There remained a dark purple colored solid, which when pulverized was dark brown in color. This compound melted at 103°.

Anal. Calcd. for $C_{16}H_{15}NBBr_2$: Br, 42.22. Found: Br, 42.25, 42.41.

This analysis shows the compound to be the dibromide of 1-phenyl-4-anilidobutadiene.

The dibromide was dissolved in chloroform and a current of ozonized oxygen passed into the solution for about twenty-four hours. The chloroform was removed by means of suction and the residual ozonide decomposed with water. It was possible to isolate

benzoic acid from the ozonization products. The benzoic acid was identified by its melting point and by the melting point of a mixture with known benzoic acid. The compound thus proves to be 1-phenyl-3,4-dibromo-4-anilido- Δ^1 -butene.

The 1-phenyl-3,4-dibromo-4-anilido- Δ^1 -butene was dissolved in chloroform and exactly one mole of bromine, dissolved in carbon tetrachloride was added. When the reaction was complete, the chloroform and the carbon tetrachloride were removed by means of suction and a purple crystalline residue remained.⁷

Anal. Calcd. for $C_{16}H_{13}NBr_4$: Br, 59.14. Found: Br, 58.94, 58.92.

The compound is the tetrabromide of 1-phenyl-4-anilidobutadiene.

The tetrabromide of 1-phenyl-4-anilidobutadiene was dissolved in chloroform and quite an excess of bromine, dissolved in carbon tetrachloride, added. The reaction mixture was allowed to stand at room temperature for about forty-eight hours. Large volumes of hydrogen bromide were evolved and crystals separated out. The crystals were collected on a filter by means of suction and washed with small amounts of chloroform. The pure white crystals which remained melted at 182° .

Anal. Calcd. for $C_{16}H_{13}NBr_8$: Br, 74.50. Found: Br, 74.62, 74.70.

The compound is the hydrogen bromide salt of 1-phenyl-1,2,3,4-tetrabromo-4-tribromoanilidobutane.

Addition of Chlorine.—The 1-phenyl-4-anilidobutadiene was dissolved in chloroform and exactly one mole of chlorine, dissolved in chloroform, was added. The reaction mixture was allowed to stand at room temperature for about twenty-four hours. The chloroform was removed by means of suction and the dark red viscous oil remaining was taken up in dry ether. The solution was filtered clear and the ether was removed from the filtrate by means of suction. The dark red viscous oil which remained was analyzed for chlorine.

Anal. Calcd. for $C_{16}H_{13}NCl_2$: Cl, 24.28. Found: Cl, 24.10, 24.12.

The compound is the dichloride of 1-phenyl-4-anilidobutadiene.

The dichloride of 1-phenyl-4-anilidobutadiene was dissolved in dry ether and dry hydrogen chloride was passed into the solution. The crystals which precipitated out were almost pure white. They were collected on a filter by means of suction, washed with dry ether to remove the excess hydrogen chloride and then dried in a vacuum desiccator over anhydrous calcium chloride. The crystals melted at 135° .

Anal. Calcd. for $C_{16}H_{13}NCl_3$: Cl, 32.39. Found: Cl, 32.55, 32.59.

The compound is the hydrogen chloride salt of the dichloride of 1-phenyl-4-anilidobutadiene.

These crystals were dissolved in chloroform and a current of ozonized oxygen passed into the solution. The chloroform was removed by means of suction and the residual ozonide decomposed with water. It was possible to isolate benzoic acid from the ozonization products. The benzoic acid was identified by its melting point and by the melting point of a mixture with known benzoic acid. The compound is therefore 1-phenyl-3,4-dichloro-4-anilido- Δ^1 -butene hydrochloride.

1-Phenyl-4-aminobutadiene.—The 1-phenyl-4-bromobutadiene was dissolved in alcohol and gaseous ammonia passed into the solution for about three days. The reaction product was diluted with a large volume of water and then extracted with ether. The ether extract was washed free of bromide ion and of ammonia and dried, first over anhydrous sodium sulfate, and then over sodium hydroxide. Dry hydrogen chloride was passed into the solution; a slightly yellow crystalline precipitate was formed. The passage of the hydrogen chloride into the solution was not carried out too long

(7) These crystals melted at $88-91^\circ$. Judging from the melting point of similar compounds described above, this melting point may be low.

lest the salt of any secondary amine be likewise precipitated. The crystals were collected on a filter by means of suction, washed with dry ether to remove the excess hydrogen chloride and then dried in a vacuum desiccator over phosphorus pentoxide. The crystals were slightly yellow and melted at 111° .

Anal. Calcd. for $C_{10}H_{12}NCl$: Cl, 19.53; N, 7.71. Found: Cl, 19.64, 19.70; N, 7.52, 7.61.

The compound is the hydrogen chloride salt of 1-phenyl-4-aminobutadiene.

The hydrogen chloride salt of 1-phenyl-4-aminobutadiene was dissolved in moist chloroform and a current of ozonized oxygen was passed into the solution. The chloroform was removed by means of suction and the residual ozonide decomposed with water. Benzoic acid was isolated from the ozonization products. The benzoic acid was identified by its melting point and by the melting point of a mixture with known benzoic acid.

Addition of Hydrogen Chloride.—The 1-phenyl-4-aminobutadiene was dissolved in dry benzene and dry hydrogen chloride was passed into the solution. A precipitate was not formed but the solution became dark red in color. Low boiling ligroin was added, drop by drop, to the solution and a chocolate brown crystalline mass was precipitated. The crystals were washed with small quantities of warm benzene and then dried on a porous plate. The crystals were slightly pink in color and melted at 138° .

Anal. Calcd. for $C_{10}H_{12}NCl_2$: Cl, 32.54. Found: Cl, 32.41, 32.38.

The structure of the compound is assumed to be 1-phenyl-3-chloro-4-amino- Δ^1 -butene hydrochloride for the same reasons as given above for 1-phenyl-3-chloro-4-anilido- Δ^1 -butene.

The 1-phenyl-4-aminobutadiene was prepared also by the following methods.

(a) An ether solution of 1-phenyl-4-bromobutadiene was introduced into a bomb tube and liquid ammonia condensed upon it. The tube was sealed and allowed to stand at room temperature for two or three days. The reaction product was worked up in a manner analogous to that described above. It was found that if sufficient alcohol were added to the tube to ensure a homogenous solution, the time of the reaction was materially shortened. It was likewise found that if the 1-phenyl-4-bromobutadiene was dissolved in alcohol, concentrated ammonium hydroxide added almost to the point of precipitating out the monobromide and the solution allowed to stand for about forty-eight hours, the 1-phenyl-4-aminobutadiene was formed.

(b) 1-Phenyl-4-bromobutadiene was dissolved in ether, a suspension of finely ground sodium amide in dry ether added and the mixture stirred mechanically. The reaction mixture was allowed to stand for eight to ten hours and the excess of sodium amide destroyed with moist ether. The reaction product was then diluted with an equal volume of ether and the solution was washed free of bromide ion and dried, first over anhydrous sodium sulfate and then over sodium hydroxide. Dry hydrogen chloride was passed into the solution and the hydrogen chloride salt of 1-phenyl-4-aminobutadiene was precipitated. Dry xylene was used to replace the ether in order that the temperature might be raised. The only result apparent was an increase in the polymerization.

The 1-phenyl-4-bromobutadiene was treated with sodium amide, dissolved in liquid ammonia, and the reaction mixture worked up as before. The 1-phenyl-4-aminobutadiene hydrochloride was isolated. Potassium amide was used with similar results.

(c) 1-Phenyl-4-bromobutadiene, in alcoholic solution, was treated with an alcoholic solution of potassium phthalimide and the reaction mixture allowed to stand at room temperature for about twenty-four hours. The reaction mixture was diluted with a large quantity of water and then extracted with ether. The ether extract was washed free of bromide ion and the ether was removed by gentle warming. The resulting residue was hydrolyzed with aqueous hydrochloric acid. The solution was then made alkaline

with sodium hydroxide and extracted with ether. The ether solution was washed free of chloride ion and dried, first over anhydrous sodium sulfate and then over sodium hydroxide. 1-Phenyl-4-aminobutadiene hydrochloride was isolated from this solution.

(d) Styrylacrylic acid, $C_6H_5CH=CH-CH=CHCOOH$, was prepared according to the method of Doebner⁸ by heating for six hours a mixture of 90 g. of cinnamic aldehyde, 90 g. of malonic acid, and 70 g. of pyridine and then pouring the reaction mixture into cold dilute sulfuric acid. The acid thus formed was purified by crystallization from dilute alcohol. The acid melted at 165°. The acid chloride of styrylacrylic acid was prepared according to the method of Rupe⁹ by heating, the acid for forty minutes with an excess of phosphorus trichloride in the presence of a small amount of dry benzene. However, it was not found necessary to isolate the acid chloride. The benzene solution of the acid chloride was poured off. Concentrated ammonium hydroxide was added to the benzene solution and then gaseous ammonia was passed into the solution for about thirty minutes. The reaction vessel was immersed in an ice-bath during the reaction. The solid that was formed was collected on a filter by means of suction and washed several times with concentrated ammonium hydroxide in order to remove any unchanged acid. The crystals which remained melted at 185°, the melting point of the acid amide of styrylacrylic acid. These crystals, in aqueous suspension, were treated with a freshly prepared 8% solution of sodium hypochlorite and the reaction mixture heated on the water-bath for six hours. The reaction mixture was then extracted with ether and the solution washed free of chloride ion. It was then dried, first over anhydrous sodium sulfate and then over sodium hydroxide. Dry hydrogen chloride was passed into the dry ether solution; the hydrogen chloride salt of 1-phenyl-4-aminobutadiene was precipitated from this solution. It is apparent that the acid amide of styrylacrylic acid has undergone a rearrangement to give 1-phenyl-4-aminobutadiene.

Summary

1. The method of preparation of 1-phenyl-4-aminobutadiene and of 1-phenyl-4-anilidobutadiene is described.
2. Both of these amines absorb hydrogen chloride in the 3,4-positions.
3. 1-Phenyl-4-anilidobutadiene absorbs both chlorine and bromine in the 3,4-positions.
4. The significance of these reactions of aliphatic amino conjugated compounds to the problem of substitution in the benzene ring is indicated.

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(8) Doebner, *Ber.*, **35**, 2137 (1902).

(9) Rupe, *Ann.*, **369**, 340 (1909).

